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AMERICAN OIL COMPANY

RESEARCH AND DEVELOPMENT DEPARTMENT

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Contract Nobr-90267
Project Serial No. SR001-03-01, Task 606

DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

BUREAU OF SHIPS
Department of the Navy
Washington, D.C.

[redacted]

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Bimonthly Progress Report No. 4
October 1, 1964 to December 1, 1964

DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

K. R. Bunting
A. M. Dobry
E. A. Swakon
P. C. Vienna
L. W. Mixon

American Oil Company
Research and Development Department
Whiting, Indiana

BUREAU OF SHIPS
Department of the Navy
Washington, D.C.

FOREWORD

This report was prepared by the Research and Development Department of the American Oil Company under U.S. Navy, Bureau of Ships Contract Nobs-90267, Project Serial No. SR001-03-01, Task 606. Covered is work done from October 1, 1964 to December 1, 1964. The work was administered under the direction of the Chief, Bureau of Ships, Code 634A, with Mr. E. C. Davis as technical monitor.

ABSTRACT

The object of this study is the development of a water-base hydraulic fluid which (1) yields a fire-resistant non-aqueous residue, (2) is compatible with materials of construction and sea-water contamination, (3) satisfactorily lubricates shipboard pumps, (4) presents no unusual storage or handling problems, and (5) exhibits no toxicological hazards under conditions of use.

Low-density polyethylene can be chlorophosphonated by reaction with phosphorus trichloride and oxygen. Hydrolysis and neutralization produces products which show considerable promise as thickeners. The product from 21,000-molecular-weight polyethylene, neutralized to a pH of 8.0 with sodium hydroxide, produces a fluid which (1) has the desired viscosity, (2) is shear stable in tests using a Raytheon Sonic Oscillator, (3) can be rendered non-corrosive to iron, copper, aluminum, zinc, and silver braise by the addition of 1.0% of sodium chromate or sodium dichromate, (4) has no deleterious effect on Buna N rubber, (5) is compatible with 10% synthetic sea water, (6) is non-toxic and non-irritating, and (7) appears to produce non-aqueous residues having satisfactory flammability characteristics. However, such a fluid, when run in a Vickers Vane pump for 141 hours at 1,000 psi and 150°F, caused excessive pump wear and loss in viscosity. There is some indication that at least a part of the loss in viscosity may have been caused by the presence of a gel in the original test fluid.

Attempts to prepare polymers of unsaturated organic acids of phosphorus having molecular weights sufficiently high to thicken water have not been successful.

DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

INTRODUCTION

Two types of fire-resistant hydraulic fluids are being used in aircraft-carrier systems. The fluid used in hydraulic catapults is a mixture of water, glycol, polyglycols, and additives. An aromatic phosphate ester fluid is used in aircraft elevators. Because of the complexity of submarine hydraulic systems, both of these fluids have serious shortcomings. The water-glycol fluids are incompatible with sea water, are relatively poor lubricants for heavily loaded bearings, and are corrosive to aluminum. In addition, loss of water results in the formation of flammable residues. Because of fluid-leakage problems, phosphate esters cannot be used in submarines.

A satisfactory water-base fluid for shipboard hydraulic-system use is needed. For the uses envisioned, fire resistance in both the finished fluid and the non-aqueous residue is of prime importance. In addition, the fluid must be capable of lubricating shipboard hydraulic pumps, be compatible with materials of construction and with 10% sea-water contamination, and present no unusual handling and storage problems. The fluid should be formulated to minimize toxicity hazards under conditions involving long periods of continuous exposure. Fluid residues should be removable by flushing with water.

In this study, the general approach consists of the synthesis and evaluation of water-soluble thickening agents which exhibit satisfactory fire-resistant properties. Development of thickening agents which allow formulation of a fluid having the desired fire-resistance, viscosity, and shear-stability characteristics will be followed by development of additives where necessary to impart satisfactory lubricating ability, oxidation and corrosion resistance, pourpoint, resistance to stable foam formation, and compatibility with sea water. When success, or near-success in the development of an appropriate thickeining agent is indicated, it will be necessary to determine the toxicological hazards which may result from use of the fluid.

EXPERIMENTAL

The current program on non-flammable hydraulic fluids is aimed primarily at the development and evaluation of a suitable water-soluble thickener which contains sufficient phosphorus to impart fire resistance to the non-aqueous residue. Two paths are being followed in an effort to develop such thickeners: (1) chlorophosphonation of polyethylene followed by hydrolysis and neutralization of the product, and (2) preparation and polymerization of unsaturated organic acids of phosphorus.

Chlorophosphonation of Polyethylene

Numerous chlorophosphonations of 21,000 m.w. polyethylene have been carried out using the procedure presented in Bimonthly Report No. 2. After hydrolysis and aging of the reaction product at 50°C, most of the product was neutralized with sodium hydroxide to produce two gallons of fluid for testing in a Vickers Vane pump. Smaller quantities were used for other studies.

Vickers Vane Pump Test - Two gallons of fluid were prepared by (1) neutralizing hydrolyzed aged product from 21,000 m.w. polyethylene with sodium hydroxide to a pH of 7.0, (2) adding water to obtain the desired viscosity, (3) adding 1% of sodium dichromate, (4) further neutralizing to a pH of 8.0 with sodium hydroxide, and (5) adding 5 p.p.m. of Union Carbide L-530 (a silicone-type foam suppressor). The resulting fluid was tested in a Vickers Vane pump for 141 hours at 1,000 psi and 150°F at a delivery rate of 1.9 gal./min. Weight-loss data obtained are:

Part	Weight Loss, gm.
No. 2015 Brass Side Plate	0.020
No. 2016 Brass Side Plate	0.025
Rotor	0.045
Ring	13.90
Vanes	0.083
Total	14.08

Other data are:

	Vis. at 150°F, SSU	pH
Initial	139.0	8.0
After Test	92.8	8

These data show that, although no substantial change in pH occurred, the wear rate was quite high and that viscosity loss was excessive.

A retained sample of the fluid used in the pump test was examined with the following results:

	Vis. at 150°F, SSU
Before pump test	139
Retained sample	118
After sonic shear*	107

* in Raytheon Sonic Oscillatory at 10,000 cycles, 0.7 R.F. Amperes at 100°F for 30 minutes.

The viscosity data appear to be unreasonable. The large difference in the viscosity of the pump-test sample and the retained sample may result because of analytical error. It may, on the other hand, result because of some gelling of the original fluid because of insufficient aging of the hydrolyzed unneutralized reaction product. Such gel formation is discussed in Bimonthly Report No. 2.

The further loss in viscosity which occurred when the retained sample was tested in the sonic oscillator does not agree with earlier data (in Bimonthly Report No. 3). This indicates that gel formation may explain the changes in viscosity.

Compatibility with Metals - Static corrosion tests at 150°F were carried out using a fluid made from 21,000 m.w. polymer neutralized with sodium hydroxide. Copper, steel, aluminum, and zinc strips were immersed in each test fluid with no effort made to prevent contact between strips. Weight-loss data are:

Inhibitor	pH	Weight Loss, $\frac{mg}{cm^2}$ After 11 Days			
		Copper	Zinc	Alum.	Steel
1.0% Sodium dichromate	8.0	0.033	0.15	0.028	0.000
1.0% Sodium dichromate	7.5	0.022	0.16	0.21	0.033
1.0% Sodium chromate	8.0	0.013	0.13	0.067	0.006
1.0% p-Nitrobenzoic acid	8.0	0.087	4.90	5.80	0.02
2.0% p-Nitrobenzoic acid	8.0	0.087	2.60	4.90	0.06
1.0% p-Nitrobenzoic acid + 1.0% Borax	8.0	0.10	3.73	2.13	0.11
1.0% p-Nitrobenzoic acid	9.0	Heavy gas evolution and precipitation			
1.0% Sodium dichromate*	8.5	0.013	0.24	0.013	0.013
1.0% p-Nitrobenzoic acid*	8.5	0.13	12.5	9.5	0.000

* 11% synthetic sea salt added.

These data indicate that the addition of 1.0% of sodium chromate or sodium dichromate results in a product which is relatively non-corrosive to metals. Contamination with 11% of synthetic sea water caused no substantial increase in corrosion rates.

p-Nitrobenzoic acid, which had shown promise in room-temperature qualitative tests, was relatively ineffective in preventing zinc and aluminum corrrosion at 150°F.

Viscosity Index - A sample of fluid from 21,000 m.w. polymer, neutralized to pH of 8.0 with sodium hydroxide, had the following viscosities:

Temp.	Vis, SSU
100°F	412.5
150°F	247.0
210°F (extrapolated)	150

The viscosity index of this sample was 153. This indicates that no difficulty should arise in meeting viscosity requirements unless the yet-to-be-developed pour depressor has a substantial adverse effect on viscosity index.

Pour Point - The sodium salt of ethane phosponic acid was insufficiently soluble in the sodium-hydroxide-neutralized fluid to be effective as a pour depressor. The minimum pour point obtained was +18°F by the addition of 10% of the sodium phosphonate.

Toxicity - As reported in Bimonthly Report No. 3, a fluid from 21,000 m.w. polymer neutralized to pH of 8.0 with sodium hydroxide is substantially nontoxic and nonirritating. A copy of the report of studies carried out by International Research and Development Corporation is attached.

Fire Resistance - In the ASTM Autogenious Ignition Test, a fluid of pH 8.0 and the same fluid with 1% sodium dichromate showed no ignition at temperatures up to 1250°F. when either the specified test amount or ten-times the specified test amount was used.

Unsaturated Acids of Phosphorus

Numerous procedures have been studied for the polymerization of dialkyl vinylphosphonates and dialkyl alkylphosphonates. In every case, either no polymer was produced or low-molecular-weight polymer was obtained.

FUTURE PROGRAM

Pump testing of fluids will continue. Two gallons of fluid thickened with the product from chlorophosphonation of 12,000 m.w. polyethylene is being prepared. Smaller amounts of fluid from 21,000 m.w. polyethylene will be prepared for shear-stability tests to determine whatever the high viscosity loss in the first pump test was caused by the presence of gel or by use of high-molecular-weight thickener.

Studies aimed at the development of non-flammable or flame-resistant pour depressors will continue. Potassium salts of alkane phosphonic acids will be tested as depressors using potassium hydroxide neutralized thickeners.

If further pump tests indicate the need, work will begin on the development of lubricity additives.

Studies aimed at the development of a procedure for producing high-molecular-weight polymers of unsaturated acids of phosphorus will continue.

International Research and Development Corporation

SPONSOR: American Oil Company

COMPOUND: LF-4581 (Water-Based Noninflammable Hydraulic Fluid).

SUBJECT: Acute Toxicity in Rats and Rabbits

Francis X. Wazeter, Ph.D.
Director of Research
International Research and
Development Corporation

Collaborators:

R. H. Buller, Ph.D., Director of Pharmacology
R. G. Geil, D.V.M., Director of Pathology

Date: October 15, 1964

I. SYNOPSIS

Compound LF-4581 was administered orally to albino rats at dosage levels extending from 250 to 10,000 mg./kg. No evidence of toxicity was observed. The LD_{50} for the test compound was in excess of 10,000 mg./kg.

When applied dermally to the prepared dorsal skin of albino rabbits in the manner described in this report, no evidence of irritation, pharmacotoxicity or mortality was observed.

The results indicate complete innocuousness to the skin of rabbits.

When LF-4581 was instilled into the eyes of albino rabbits in the manner described herein, no evidence of irritation occurred, therefore compound LF-4581 is considered to be non-irritating to the eyes of albino rabbits.

II. COMPOUND

The test compound was received from the American Oil Company, Chicago, Illinois on August 29, 1964. It was a viscous brown fluid in a glass bottle identified as "LF-4581; Water-based Non-flammable Hydraulic Fluid; Contract No. NOBS 90267; L. W. Mixon".

For the purpose of these studies the test compound was considered to be free of impurities.

III. ACUTE ORAL TOXICITY (LD_{50}) IN FEMALE ALBINO RATS

A. METHOD:

Female Charles River albino rats weighing from 215 to 280 grams were used. The test compound was administered orally by

gavage, to 6 rats per dosage level at 250, 500, 1000, 2500, 5000 or 10,000 mg./kg.

Food was withheld from all of the animals for three to four hours prior to administration of the compound. After administration of the compound the animals were housed throughout a 14-day observation period in individual metal cages suspended above the dropping with food and water available ad libitum.

The rats were observed for mortality and pharmacotoxic signs at the following time intervals: 0-60 min., 60-120 min., 120-240 min., 24 hours, and daily thereafter for 13 days.

The test compound was administered undiluted at volumes commensurate with each respective dosage level and the individual body weight of the animals.

B. RESULTS:

1. Pharmacotoxic Signs:

No pharmacotoxic or toxic signs were observed at any dosage level which could be attributable to an effect of the test compound. All animals gained weight normally throughout the experimental period.

2. Mortality:

No animals died at any of the dosage levels tested.

3. Acute Toxicity (LD_{50}):

From the results obtained the LD_{50} for LF-4581 would be in excess of 10,000 mg./kg. These findings indicate that LF-4581 is a nontoxic substance.

IV. ACUTE DERMAL TOXICITY (LD_{50}) IN THE ALBINO RABBIT

A. METHOD:

Twelve albino rabbits undifferentiated as to sex and weighing from 2123 to 2913 grams were used. The dorsal skin was prepared for the dermal application of the test compound by close clipping of the hair from the back and flanks of each animal with an electric clipper. The skin of one-half of the animals was further prepared by making longitudinal epidermal abrasions through the stratum corneum with a scalpel blade. The rabbits were placed in stocks and LF-4581 was applied once only to the backs of 4 rabbits per dosage level at dosages of 0.5, 1.0 or 2.0 grams/kg., and the body of each rabbit was wrapped with bandage.

After a 24-hour period of exposure to the test compound the the bandages were removed, the back of each animal was wiped dry and the degree of irritation scored. The rabbits also were observed for evidence of mortality and pharmacotoxic effects and returned to their individual cages for observation for a 13-day period.

During the period of observation all of the rabbits were observed once daily for evidence of dermal irritation, death and pharmacotoxic signs. Food and water were available ad libitum throughout the observation period.

Dermal irritation was scored according to the method of Draize on the following page.

CODE

Erythema:

0 - None
1 - Very slight to slight
2 - Well defined or moderate
3.- Severe or marked

Eschar not graded only recorded same as necrosis, blanching, and hemorrhagic areas.

Edema:

0 - None
1 - Very slight to slight
2 - Moderate (raised 1.0 to 10 mm.)
3 - Marked (raised $\geq$ 10.00 mm.)

Atonia:

1 - Slight (sl. impairment of elasticity)
2 - Moderate (slow return to normal)
3 - Marked (no elasticity)

Desquamation:

1 - Slight (slight scaling)
2 - Moderate (scales and flakes)
3 - Marked (pronounced flaking with denuded areas)

Coriaceousness:

1 - Slight (decrease in pliability)
2 - Moderate (leathery texture)
3 - Marked (tough and brittle)

Fissuring:

1 - Slight (definite cracks in epidermis)
2 - Moderate (cracks in dermis)
3 - Marked (cracks with bleeding)

B. RESULTS:

The results of this experiment were essentially negative. One rabbit at the 1.0 gm./kg. dosage level exhibited a very mild erythema at 24 and 48 hours after application of LF-4581. All rabbits gained weight normally during the observation period.

Due to the negative results obtained, a table of scores is not included in this report.

According to the results, LF-4581 does not cause skin irritation, nor does its contact with the skin in the manner described cause evidence of adverse systemic effects or mortality.

V. PRIMARY SKIN IRRITATION IN THE RABBIT

A. METHOD:

Six albino rabbits undifferentiated as to sex and weighing from 2203 to 2859 grams were used. The dorsal skin of each animal was prepared for the dermal application of the test compound by clipping an area approximately 3 inches square. The skin of one-half of the animals was further prepared by making longitudinal abrasions with a scalpel blade through the stratum corneum.

The rabbits were placed in stocks and LF-4581 was applied once only to the prepared skin of the animals at a dosage of 0.5 ml./rabbit. The area was then covered with dental dam and gauze and the body of each rabbit was wrapped with elastic bandage.

After a 24-hour period of exposure to the test compound the bandages were removed and the degree of irritation (erythema and edema) recorded. The rabbits were then returned to their individual cages and the skin of each animal again observed and the irritation

scored at 72 hours.

The method of scoring used was according to the following table (Draize):

Erythema:

0 - None
1 - Very slight to slight
2 - Well defined or moderate
3 - Severe or marked

Eschar not graded only recorded same as necrosis, blanching, and hemorrhagic areas.

Edema:

0 - None
1 - Very slight to slight
2 - Moderate (raised 1.0 to 10 mm.)
3 - Marked (raised $>$10.0 mm.)

L. RESULTS:

Four-of-six rabbits exhibited a very mild degree of erythema at the 24-hour period of observation. One-of-six still exhibited a very mild erythema at 72 hours. No evidence of moderate to severe erythema was evidenced. Edema did not occur.

The results of this test indicate that LF-458i is not a primary irritant.

A table of scores has not been included because of the essentially negative results obtained.

VI. EYE IRRITATION TEST IN THE ALBINO RABBIT

A. METHOD:

Six albino rabbits undifferentiatd as to sex and weighing from

2.0 to 3.0 kg. were used. Throughout the study period the rabbits were individually housed in metal cages suspended above the droppings. Food and water were available ad libitum.

One-tenth milliliter of LF-4581 was instilled into the conjunctival sac of one eye of each rabbit. The opposite eye served as the untreated control. Prior to instillation of the test compound, and again at termination of the 72-hour observation period, both eyes of each animal were examined with the use of 2.0 per cent sodium fluorescein and a small-window ultraviolet pencil lamp. Other observations for eye irritation were made at 24, 48 and 72 hours. Eye irritation was graded and recorded according to the Scale for Scoring Ocular Lesions on the following page.

B. RESULTS:

The results of this test were essentially negative. No irritation of any nature was observed of the treated eyes of any of the rabbits in this study. Due to the results obtained a table of scores has not been included in this report.

LF-4581 is considered to be nonirritating to the eye when applied in the manner described in this report.

Scale for Scoring Ocular Lesions*

(1) Cornea

(A) Opacity-degree of density (area most dense taken for reading)

No Opacity	0
Scattered or diffuse area, details of iris clearly visible	1
Easily discernible translucent areas, details of iris slightly obscured	2
Opalescent areas, no details of iris visible, size of pupil barely discernible	3
Opaque, iris invisible	4

(B) Area of cornea involved

One quarter (or less) but not zero	1
Greater than one quarter, but less than half	2
Greater than half, but less than three quarters	3
Greater than three quarters, up to whole area	4

Score equals A x B x 5 Total maximum = 80

(2) Iris

(A) Values

Normal	0
Folds above normal, congestion, swelling, circumcorneal injection (any or all of these or combination of any thereof) iris still reacting to light (sluggish reaction is positive)	1
No reaction to light, hemorrhage, gross destruction (any or all of these)	2

Score equals A x 5 Total maximum = 10

(3) Conjunctivae

(A) Redness (refers to palpebral and bulbar conjunctivae excluding cornea and iris)

Vessels normal	0
Vessels definitely injected above normal	1
More diffuse, deeper crimson red, individual vessels not easily discernible	2
Diffuse beefy red	3

(B) Chemosis

No swelling	0
Any swelling above normal (includes nictitating membrane)	1
Obvious swelling with partial eversion of lids	2
Swelling with lids about half closed	3
Swelling with lids about half closed to completely closed	4

(C) Discharge

No discharge	0
Any amount different from normal (does not include small amounts observed in inner canthus of normal animals)	1
Discharge with moistening of the lids and hairs just adjacent to lids	2
Discharge with moistening of the lids and hairs, and considerable area around the eye	3

Score equals (A + B + C) x 2 Total maximum = 20

The maximum total score is the sum of all scores obtained for the cornea, iris, and conjunctivae. Total maximum score possible = 110.

* Lehman, A. J et al., Appraisal of the Safety of Chemicals in Foods, Drugs, and Cosmetics, Assoc Food and Drug Officials of the U. S., Austin, Texas, 1959.